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# Modification of the Versatile Aerosol Concentration Enrichment System (VACES) for conducting inhalation exposures to semi-volatile vapor phase pollutants

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## ABSTRACT

A novel sampling system was developed to provide concentrated vapor phase only semi-volatile organic species for in-vivo exposure studies. The system consists of two units: particles (including their semi-volatile component) are first concentrated by means of the Versatile Aerosol Concentration Enrichment System (VACES), and subsequently drawn through a heating section, in which semi-volatile particle-bound components partition to the gas phase, while non-volatile particles are removed by a quartz filter placed after the heater. The vapors are then cooled to ambient temperatures, without producing nano-particles by nucleation, and can be readily used for exposure studies. Laboratory tests were carried out at various heater temperatures using ammonium sulfate, adipic acid and glutaric acid to investigate the occurrence of nucleation in the cooling section. Subsequently the system was tested in the field with concentrated particle and vapor samples taken upstream of the heater, immediately downstream of the filter, and after the cooling section. Chemical analysis of particle and vapor phases upstream and downstream of the system was conducted for selected polycyclic aromatic hydrocarbons (PAHs), and showed very good PAH recovery. These tests indicate that the modified VACES-heater-filter (VHF) system can provide concentrated PM (including their semi-volatile compounds) and PM-bound semi-volatile species purely in the vapor phase for inhalation exposure studies separately, a feature that makes this system an attractive approach for toxicity studies, particularly in light of the increasing interest in health effects of exposures to multi-pollutant atmospheres.

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## 1. Introduction

In the last decades, a number of epidemiological and toxicological studies have demonstrated robust associations between exposure to ambient particulate matter (PM) and increased cardiopulmonary morbidity and mortality (Casssee et al., 2005; Dockery et al., 1993; Laden et al., 2000; Peters & Pope, 2002; Schulz et al., 2005; Smith et al., 2003; Zelikoff et al., 2003). Ambient PM is a complex mixture of chemical constituents originating from a variety of primary sources as well as by atmospheric transformations of gas precursors. Major components that contribute to the multi-pollutant atmosphere include inorganic compounds (i.e., sulfate, nitrate and ammonium ions), trace metals and elements, and

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elemental carbon and organic carbon (EC and OC). The latter comprised of non-volatile as well as semi-volatile species that are in dynamic equilibrium with their vapor phase in the atmosphere (Ning & Sioutas, 2010). The photo-oxidation of gas precursors in the atmosphere, such as volatile organic compounds (VOCs), promotes the formation of secondary organic aerosols (Robinson et al., 2007). Recent studies indicate that semi-volatile organic compounds (SVOC), initially bound to the particulate phase, partition to the vapor phase as a result of atmospheric dilution following their release in the atmosphere; subsequent photo-oxidation of these low volatility vapors may contribute to substantial formation of secondary organic aerosols (SOAs) (Robinson et al., 2007). These findings emphasize the complex and dynamic behavior of ambient PM, especially those produced from combustion processes in the atmosphere.

Recent studies have linked individual particle chemical components with different adverse health effects (Gerlofs-Nijland et al., 2009). Of particular note is the role of SVOC and VOCs due to their toxic potency, including the capability to induce cellular oxidative stress (Baltensperger et al., 2008; Delfino et al., 2009; Ntziachristos et al., 2007) and consequently adverse health effects (Arif & Shah, 2007; Boeglin et al., 2006; Rumchev et al., 2004). For example, polar organic compounds such as quinones are reported to act as catalysts to directly produce reactive oxygen species (ROS), resulting in oxidative stress (Kumagai et al., 1997; Squadrito et al., 2001); polycyclic aromatic hydrocarbons (PAHs) can induce oxidative stress indirectly, through their biotransformation to generate redox active quinones (Penning et al., 1999). VOCs concentration levels in the ambient air have been linked to the incidence of chronic respiratory symptoms (Ware et al., 1993) and the frequency of hospital admissions due to ischemic heart disease and myocardial infarctions (Gordon et al., 1998; Klemm et al., 2004; Tolbert et al., 2001). In a recent exposure study of freeway traffic emissions on the cardiovascular effects of rats, vapor-phase components, rather than PM, were associated with a decrease in heart rate variability (Elder et al., 2007).

Although the association of adverse health effects with semi-volatile and/or volatile organic compounds has been reasonably well documented, the importance of the specific phase of the SVOC on toxicity remains to be investigated. For example, it is unclear whether the same SVOC species would elicit similar health effects if inhaled as a pure vapor as opposed to bound to ambient PM. A recent study by Figuren-Fernandez et al. (2010) assessed the redox and electrophilic potential of particle- and vapor-phase components of ambient aerosols using different chemical assays, and found differential distribution of redox activity and electrophiles between the two phases, underscoring the significance of vapor phase components in exposure and the need for health and risk assessment studies that include both particles and vapors when assessing the overall toxic potency of ambient aerosols. In recent studies by our group, we evaluated the redox properties of the semi-volatile component of PM in dynamometer, roadway tunnel and ambient settings (Biswas et al., 2009; Verma et al., 2011). Verma et al. (2011) demonstrated that over 60–90% of the overall redox activity of the sampled PM was indeed associated with these semi-volatile components, thereby underscoring their intrinsic toxicity and overall importance in understanding the health effects of air pollution.

In the previous investigations, the Versatile Aerosol Concentration Enrichment System (VACES), designed and engineered by University of Southern California (Kim et al., 2001a, 2001b), has been used in tandem with commercially available thermodenuder (Dekati Ltd., Finland) to remove semi-volatile PM species from the particle phase and provide non-volatile PM for chemical and toxicological studies (Verma et al., 2011). In the present study, the thermodenuder was modified by replacing the adsorption section with a newly designed filter holder, and tested in tandem with the VACES in order to separate semi-volatile species from the particle phase, and provide them in vapor phase for inhalation exposure studies. Laboratory tests were carried out with selected aerosols of diverse volatility to characterize the optimal operating temperatures and flow settings of the system. Time-integrated field tests in an urban environment were also conducted to evaluate its performance with atmospheric aerosols in ambient conditions.

## 2. Experimental methodology

### 2.1. Design of the VACES-heater-filter (VHF) system

The VACES-heater-filter (VHF) system is comprised of two modules: the Versatile Aerosol Concentration Enrichment System (VACES) and a heater equipped with a quartz filter, modified from a commercially available thermodenuder. The two major components of the system are described below.

#### 2.1.1. Versatile Aerosol Concentration Enrichment System (VACES)

The VACES is a particle concentrator technology whose laboratory and field characterization are described in detail by Khlystov et al. (2005) and Kim et al. (2001a, 2001b). Briefly, the sampled aerosol is drawn inside a saturator and mixed with ultrapure deionized water vapor to achieve saturation, and then it passes through a cooling section that induces condensational growth of the particles to super-micrometer size via supersaturation. The grown particles are then concentrated by virtual impaction. The VACES employs three virtual impactors in parallel, concentrating particles from a total flow of  $300\text{ L min}^{-1}$  to a flow of  $15\text{ L min}^{-1}$  ( $5\text{ L min}^{-1}$  through each of the virtual impactors); hence achieving the overall theoretical concentration enrichment factor of 20 times.

### 2.1.2. Heating and filtration unit

In order to separate the non-volatile particles from the semi-volatile vapors, a commercially available thermodenuder (TD; Model ELA-230, Dekati Ltd., Finland) was modified as follows. The Dekati thermodenuder consists of a heater module, followed by a cooling/adsorption unit. In the original design, the volatile/semi-volatile fraction of the ambient aerosol stream is evaporated in the heating section, and then adsorbed on the activated carbon in the cooling/adsorption section, leaving the non-volatile fraction of PM to pass through the system. For the purposes of this study, the cooling/adsorption section was removed, and a newly designed filter holder was inserted and sealed within the heater. During heating, semi-volatile aerosols partition to the vapor phase. The non-volatile particles are collected onto a pre-baked (550 °C) quartz filter (Quartz microfiber filters, Whatman International Ltd., UK), placed inside a filter holder, while semi-volatile vapors pass through the filter with the air stream. The quartz filter is placed inside the heater to minimize the condensation of gaseous semi-volatile species on the filter. Subsequently, the particle-free semi-volatile vapor stream is drawn through a cooling section, in which the stream temperature is reduced to ambient temperatures ( $\sim 25$  °C).

## 2.2. Experiment setup

The VHF tandem system was tested in the laboratory using different types of aerosols and in the field experiments with ambient aerosols. The VACES configured in tandem with the commercially available Dekati thermodenuder has been already used by our group to separate non-volatile PM components from the total concentrated aerosol stream (Biswas et al., 2009; Verma et al., 2011). In the present study, the VACES was configured in tandem with the heating and filtration unit modified from the Dekati thermodenuder as described above. Continuous particle measurement instruments were deployed to measure particle size distributions and number concentrations before and after the modified VACES. Subsequently, the sampling system was deployed in the field to be tested with ambient urban PM, in conjunction with time-integrated and continuous monitors.

### 2.2.1. Test particles and instrumentation

The goal of the VHF tandem system is to partition PM-bound semi-volatile species to the gas phase by heating concentrated ambient aerosols, and separate the non-volatile particles from the semi-volatile vapors while suppressing particle formation by nucleation of these vapors as they are cooled to ambient temperatures. The vapor phase of semi-volatile species can subsequently be used in in-vivo inhalation exposures. The most critical feature in the selection of operating parameters of this system is the choice of a temperature that maximizes the partitioning of semi-volatile species to the gas phase, while avoiding nucleation of the particle-free semi-volatile vapors in the cooling section. Intuitively speaking, the higher temperature values will maximize the partitioning of SVOC to the vapor phase; however, higher temperatures will also cause volatilization of very low volatile PM compounds, which will readily nucleate during cooling.

Laboratory experiments were carried out at various temperature settings using three types of polydisperse aerosols: ammonium sulfate, adipic acid, and glutaric acid. The Dekati thermodenuder can operate in temperatures as high as 300 °C. Laboratory experiments were conducted in the temperature range 100–250 °C. Aerosols were generated by atomizing dilute aqueous analyte suspensions of these species in ultrapure deionized water, using a commercially available nebulizer (VORTAN Medical Technology, Inc., Sacramento, CA, USA) in a process described in detail by Misra et al. (2001). Following atomization, the aerosol was diluted with a dry, particle-free air stream. Ammonium sulfate was selected because it represents one of the most predominant inorganic salts in ambient PM<sub>2.5</sub> (Malm et al., 2004; Sardar et al., 2005) and it is among the most stable semi-volatile species in the atmosphere due to its relatively low volatility (Scott & Cattell, 1979). Adipic acid and glutaric acid are dicarboxylic acids found in ambient organic aerosols, and were chosen to represent typical products of secondary aerosol formation by photo-oxidation of organic gaseous precursors (Cruz & Pandis, 1999; Sempere & Kawamura, 1994). Both of these organic aerosols are water soluble and more volatile than ammonium sulfate.

Fig. 1 shows the schematic of the laboratory test setup. A Scanning Mobility Particle Sizer (SMPS Model 3096, TSI, Inc., Shoreview, MN, USA) with a Differential Mobility Analyzer (DMA, Model 3080L, TSI Inc., Shoreview, MN, USA) in combination with a TSI Condensation Particle Counter (CPC 3022, TSI, Inc., Shoreview, MN, USA) was used for the measurement of particle size distributions upstream, downstream of the heater, and after the cooling section. A quartz filter was placed immediate downstream of the heater. The SMPS sample and sheath air flows were adjusted to measure the particle size distribution in the range 5.9–224.7 nm in mobility diameter. For all the test aerosols, the volatility measurements were made at a flow rate of 10 L min<sup>−1</sup> and the heater temperature was gradually increased in 10 °C increments, covering the temperature range 50–250 °C. The air stream temperature was reduced to ambient levels ( $\sim 25$  °C) in the cooling section for all heater temperature settings.

Particle losses in the system were evaluated first without heating the aerosols, by measuring the particle size distributions at the inlet and exit of the system. These tests showed minimal diffusion losses, with particle number loss of less than 5% for 20 nm particles at 10 L min<sup>−1</sup>, and lower losses for larger particles (data not shown), consistent with theoretical predictions (Baron & Willeke, 1992).

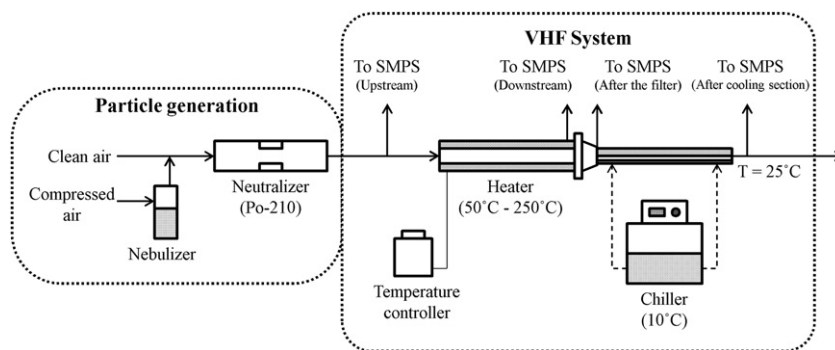


Fig. 1. Schematic of laboratory test setup.

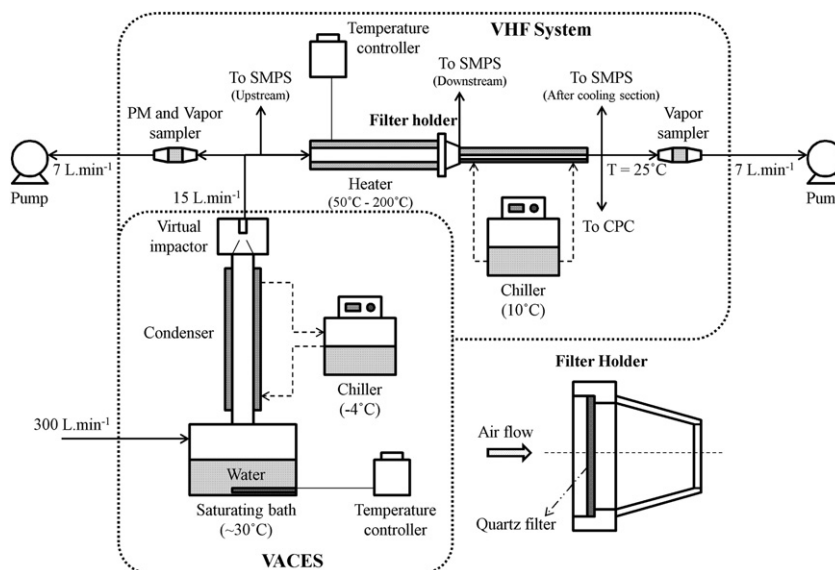


Fig. 2. Schematic of field test setup and the filter holder.

### 2.2.2. Field tests

Following the laboratory experiments, the VHF system was deployed in an urban area adjacent to main campus of the University of Southern California (USC), about 150 m west and downwind of a major freeway (I-110), with high light and heavy duty traffic, and about 3 km south of downtown Los Angeles, CA, USA. The proximity to I-110 freeway ensures the presence of high concentrations of freshly emitted semi-volatile organic species (e.g., polycyclic aromatic hydrocarbons, PAHs) (Eiguren-Fernandez et al., 2004). A detailed schematic of the experimental setup is shown in Fig. 2. Time-integrated samples were collected upstream of the system, immediate after the filter-equipped heater and downstream of the cooling section. A sampling matrix comprising of a 47 mm quartz fiber filter (Pall Corp., NY, USA) and 20 g of XAD-4 resin (Acros Organics, NJ, USA) was used to collect particle- and vapor-phase PAHs, respectively. Previous studies have shown that this amount of XAD (Eiguren-Fernandez et al., 2003) yields a collection efficiency of  $\sim 99\%$  for the target vapor phase PAHs. The XAD-4 resin was held in a glass cylinder between two 400-mesh stainless steel screens. The XAD-4 resin and the quartz filters were pre-cleaned prior to sampling, following procedures reported elsewhere (Eiguren-Fernandez et al., 2004). The matrices were kept at  $-20^\circ\text{C}$  before and after sampling. The quartz filter after the heater was removed and stored in  $-20^\circ\text{C}$  and a new filter was used at the beginning of each sampling day to minimize the possibility of volatilization of the collected semi-volatile species. Lab and field blanks were used during the study for quality control. All reported PAH concentrations are adjusted for laboratory and field blanks. A small flow of 0.3 LPM at the exit of the VHF and before the XAD sampler was drawn into a CPC (Model 3022A, TSI Inc., Shoreview, MN, USA) throughout the experiments to monitor on line particle concentration and confirm that no nucleation occurs during the field experiments.

### 2.2.3. Chemical analysis

The quartz filters and the XAD-4 resin were extracted by ultrasonication for two periods of 15 minutes each using 15 and 80 mL of a mixture of dichloromethane:acetonitrile (2:1 v/v), respectively. The extracts were filtered using a

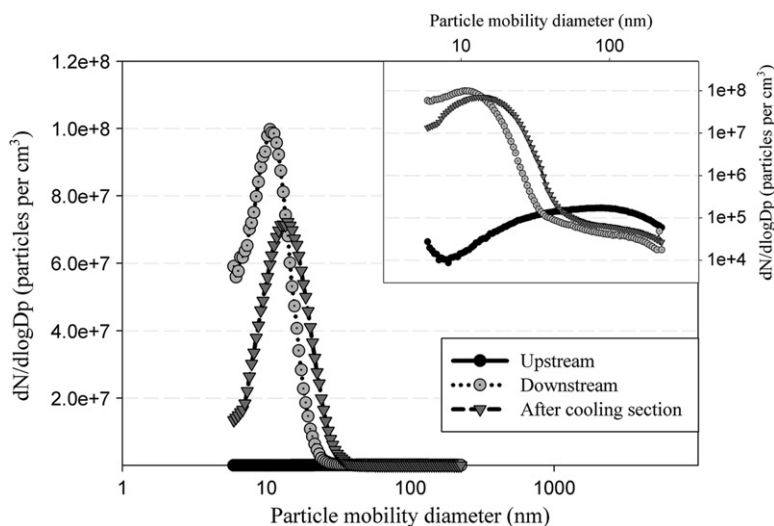
Millipore vacuum system (Millipore Corporation, Bedford, MA, USA) and 1 mL aliquots were taken from the vapor-phase extract for low molecular weight PAH analysis (naphthalene, acenaphthene and fluorene). The remaining extract of the vapor-phase sample and the particle-phase extract were volume reduced to  $\sim 100 \mu\text{L}$  for the quantification of rest of the PAHs. The entire extraction process was performed under yellow light condition using amber glass vials to avoid photodecomposition. Field blanks were extracted and analyzed for every ten samples. Details of extraction and PAH quantification process using HPLC are described by [Figuren-Fernandez et al. \(2003\)](#). Results were only reported if the signal to noise ratios were higher than 3. SRM 1649a (NIST) was used to determine the analytical procedure precision (4.2%) and PAH extraction recovery efficiency (92–97%).

### 3. Results and discussion

#### 3.1. Laboratory evaluation of the system

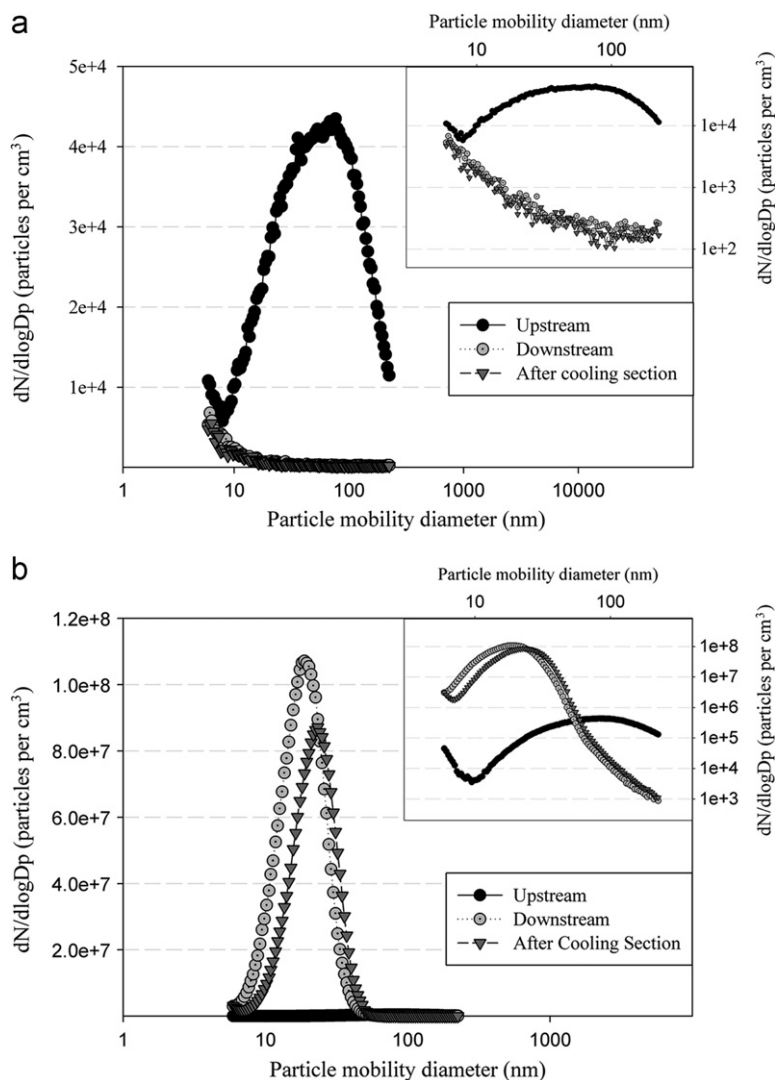
[Fig. 3](#) shows the particle size distributions of ammonium sulfate measured at upstream, downstream of heater without the filter, and after the cooling section at  $150^\circ\text{C}$ . Heating the aerosol to temperatures below  $100^\circ\text{C}$  had negligible effects on particle size distribution; however as the temperature increases to  $100^\circ\text{C}$  and beyond, ammonium sulfate particles start evaporating, with the mode diameter in the number distribution decreasing, as a result of particle shrinkage. As shown in [Fig. 3](#), heating the aerosols to  $150^\circ\text{C}$  causes substantial shrinkage, accompanied by a considerable increase in total number concentration (from  $4.7\text{e}4$  particles/ $\text{cm}^3$  upstream of the heater to  $1.8\text{e}6$  particles/ $\text{cm}^3$  to downstream of the heater and  $2.2\text{e}7$  particles/ $\text{cm}^3$  after the cooling section, respectively), a clear indication of nucleation occurring after cooling. It should be noted that the volatility characteristics of any type of aerosols determined by thermodenuders or similar experimental approaches depend on the residence time of the particles in the heating section of the device. [An et al. \(2007\)](#) and [Wu et al. \(2009\)](#) reported lower temperatures for evaporation of ammonium sulfate particles, however both experiments were conducted at relatively lower flow rates, thus with longer residence times in their thermodenuders.

When the quartz filter was placed after the heating section, over 98% of particles by number were removed. In addition to these measurements, the particle size distribution and number concentration were also monitored downstream of the cooling section, since the accumulated ammonium sulfate vapor after heating may pass through the filter and undergo nucleation during rapid cooling. To investigate the occurrence of nucleation, the heater temperature was increased stepwise, while the cooling section temperature was kept at  $25^\circ\text{C}$  in all experiments. No nucleation was observed with the heater temperatures set as high as  $150^\circ\text{C}$ ; however nucleation became evident when the heater temperature reached  $170 \pm 10^\circ\text{C}$  in repeated experiments. [Fig. 4a](#) and [b](#) shows the size distribution of ammonium sulfate particles measured upstream and downstream of the heater, and after the cooling section at  $150$  and  $170^\circ\text{C}$ , respectively. At  $150^\circ\text{C}$ , the particle number loss immediately after filter and after the cooling section was 96.3% and 97.0%, respectively, indicating no nucleation ([Fig. 4a](#)). However, at  $170^\circ\text{C}$  and above, nucleation is clearly evident after cooling, with the number concentration being significantly higher than the upstream concentration. The particle concentration immediately after the filter was  $4.1\text{e}7$  particles/ $\text{cm}^3$  with a mode diameter of  $\sim 17$  nm at  $170^\circ\text{C}$ . The number concentration after the cooling section decreased to  $3.2\text{e}7$  particles/ $\text{cm}^3$  with the mode diameter at  $\sim 21$  nm ([Fig. 4b](#)), while the particle volume concentration increased from  $2.09\text{e}11$   $\text{nm}^3/\text{cm}^3$  after the filter to  $2.74\text{e}11$   $\text{nm}^3/\text{cm}^3$  downstream of the cooling section. Our



**Fig. 3.** Particle size distributions of ammonium sulfate at  $150^\circ\text{C}$  with no filter after the heater. Same figure presented in the inset in logarithmic scale.

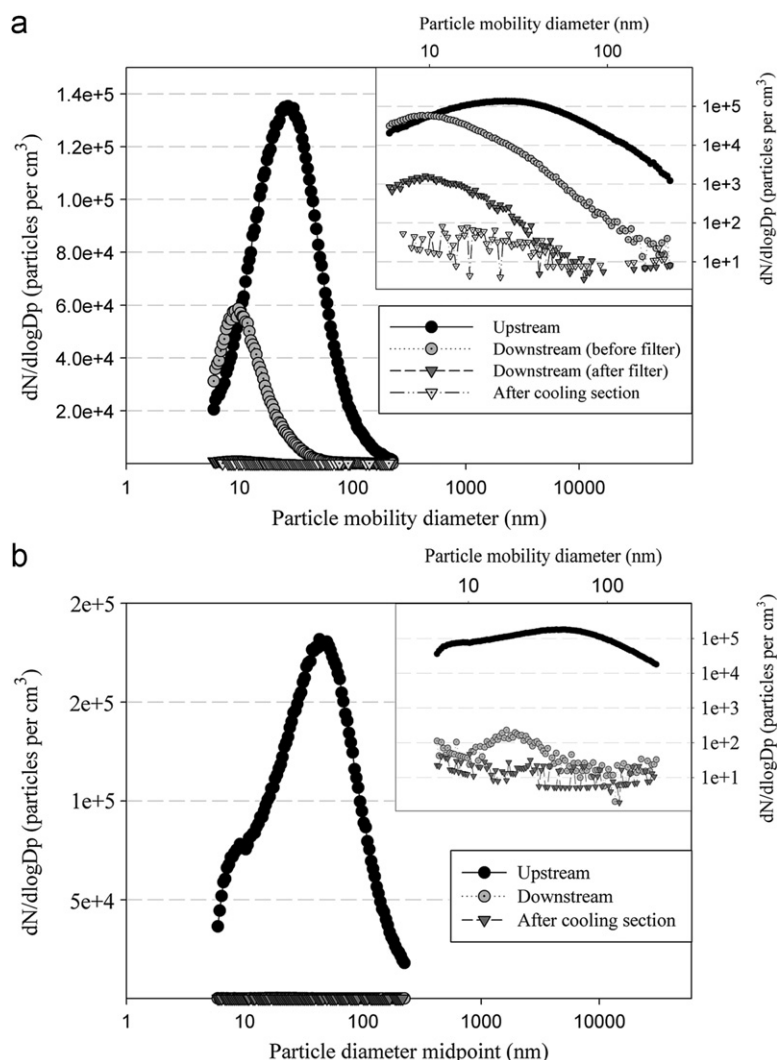




**Fig. 4.** (a) Particle size distributions of ammonium sulfate at 150 °C. Same figure presented in the inset in logarithmic scale. (b) Particle size distributions of ammonium sulfate at 170 °C. Same figure presented in the inset in logarithmic scale.

observations are consistent with previous studies (Burtscher et al., 2001) reported that ammonium sulfate starts evaporating at about 115 °C, with a significant loss in particle volume at 160 °C. (Clarke, 1991) showed that ammonium sulfate starts evaporating slowly at about 150 °C but remains unaffected at temperatures below 150 °C. The slight differences in these observations may be due to different residence times in the heating sections of the particular experimental setups, as we discussed earlier.

Similar tests were also carried out using adipic and glutaric acids, both of which are more volatile than ammonium sulfate, and higher heater temperatures would be required to induce their nucleation in the cooling section. With the stepwise increasing of heater temperature from 50 to 250 °C, no sign of nucleation was observed in the VHF system for adipic acid. Fig. 5a shows the particle size distributions obtained for adipic acid at 100 °C. The total number concentrations of aerosolized acids were set to approximately  $\sim 1e5$  particles/cm<sup>3</sup> in the upstream, in the range of typical concentration-enriched ambient aerosols achieved by the VACES. Fig. 5a presents the number size distribution of adipic acid aerosols measured at upstream, downstream of the heater, immediately after filter, and after the cooling section with the heater temperature set at 100 °C. Substantial particle shrinkage by evaporation is evident after heating, with a particle number concentration reduction by 73.3%, from  $1.0e5$  particles/cm<sup>3</sup> upstream to  $2.7e4$  particles/cm<sup>3</sup> downstream of the heater, and before the filter. Particle evaporation is also accompanied by a change in the particle size distribution mode diameter from 60 nm upstream to 20 nm downstream of the heater. The particle number concentrations downstream of the filter and after the cooling section were negligible (632 and 36 particles/cm<sup>3</sup>) indicating more than 99% of particle were removed by the filter and the subsequent cooling did not induce any nucleation. Similar results were also observed for glutaric acid at a temperature range 50–220 °C. Fig. 5b shows particle size distributions at the heater temperature of



**Fig. 5.** (a) Particle size distributions of adipic acid at 100 °C. Same figure presented in the inset in logarithmic scale. (b) Particle size distributions of glutaric acid at 200 °C. Same figure presented in the inset in logarithmic scale.

200 °C with significant reduction of the particle number concentrations after the heater as well as after the cooling section. During continued heating from 220 to 250 °C, nucleation began after the cooling section. These data are not shown here, since these temperatures far exceed the range tested for the optimization experiments of the system.

### 3.2. Field test of the system for optimization of operational temperature

The particle size distribution and number concentrations of the urban aerosols at different sampling points of the VHF were measured by the SMPS during the field test of the system, as shown in Fig. 2. The heater temperature was gradually increased from 50 to 200 °C similar to the approach for laboratory tests, and no nucleation was observed at heater temperatures up to 150 °C. Fig. 6 shows the number size distributions before and immediately after the heater, and also after the cooling section of the system at 150 °C. The particle loss after the heater and after the cooling section was 99.8% and 99.9%, respectively. As the heater temperature continued to increase, a slight increase of particle number concentration was detected by the SMPS, while increasing the heater temperature to beyond 170 °C induced a noticeable increase in particle number concentrations. Fig. 7 shows the size distribution at 170 °C at different measurement points of the system. While there are no signs of nucleation immediately after the quartz filter, nucleation is evident after the cooling section, producing particles smaller than 10 nm. The total number concentration after the VACES was  $1.72 \times 10^5$  particles/cm<sup>3</sup>, while the number concentration dropped to  $1.75 \times 10^2$  particles/cm<sup>3</sup> immediately after the filter and  $1.28 \times 10^4$  particles/cm<sup>3</sup> after the cooling section, resulting in 99.9% and 92.6% particle loss, respectively. Similar results were observed in subsequent tests, with nucleation occurring in the temperature range of 160–200 °C. Based on the laboratory

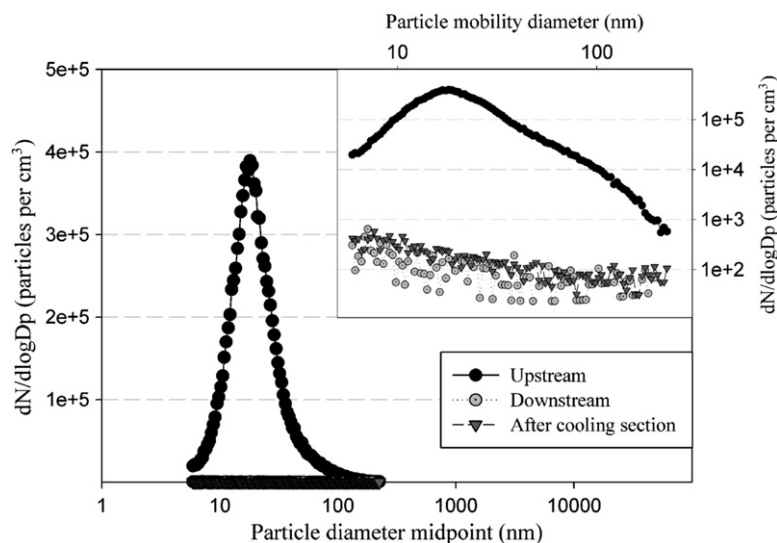


Fig. 6. Particle size distributions of concentrated ambient particulate matter at 150 °C. Same figure presented in the inset in logarithmic scale.

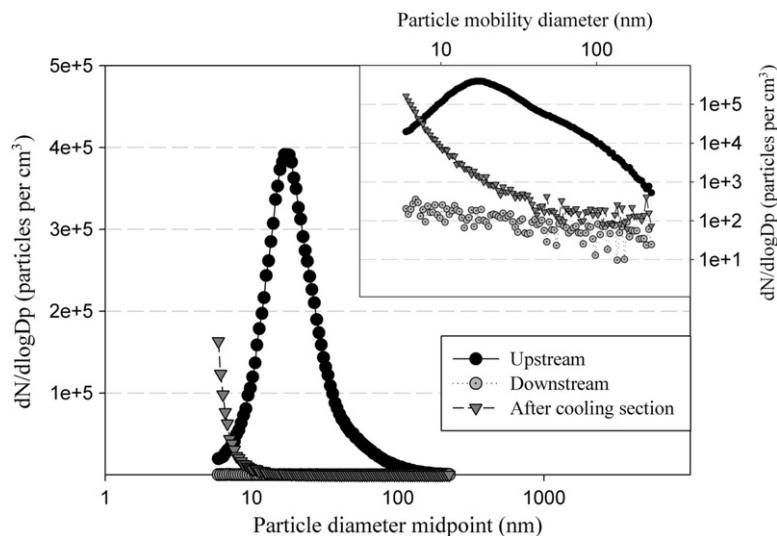


Fig. 7. Particle size distributions of concentrated ambient particulate matter at 170 °C. Same figure presented in the inset in logarithmic scale.

and field tests, 120 °C was chosen as the optimal heater temperature, maximizing the partitioning of semi-volatile species to the vapor phase while preventing nucleation of less volatile and more stable atmospheric species (e.g., ammonium sulfate), in the cooling section of the system. This was the temperature at which the time integrated field tests were conducted, described in the following section.

### 3.3. Time integrated measurements of particle and vapor phases polycyclic aromatic hydrocarbons (PAHs)

In order to evaluate the effectiveness of the VHF system to partition semi-volatile PM-bound species from the particulate to the vapor phase without nucleation, time-integrated measurements of both particle and vapor phase PAHs at different parts of system were conducted. The sampling points upstream of the VHF, immediately after the heater, and downstream of the cooling section, using XAD samplers and/or filters, are shown in Fig. 2. The collected samples were analyzed for 11 priority pollutant polycyclic aromatic hydrocarbons (PAHs—Table 1), as discussed earlier. During the time-integrated sampling period, particle number concentration after the cooling section was monitored continuously; the measured concentrations were generally below 10 particles/cm<sup>3</sup> throughout the course of sampling, indicating that no nucleation occurred.

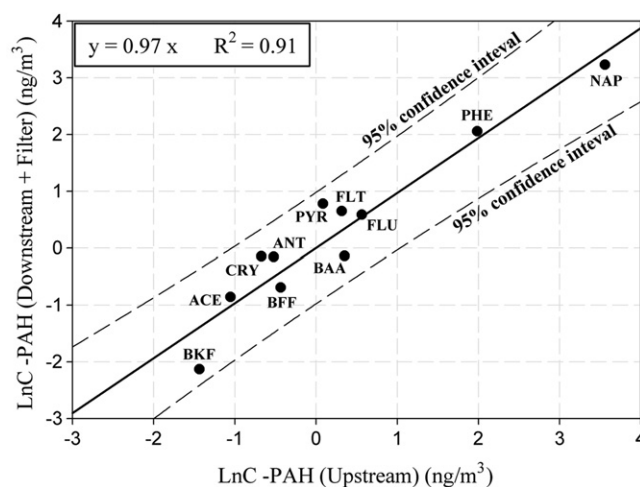
Samples collected upstream of the VHF include both particle and vapor phase of the PAHs, captured on the filter and XAD sampler, respectively. Upon heating at 120 °C, the particle phase semi-volatile PAHs evaporate and partition to their



**Table 1**

PAH codes, molecular weights, subcooled liquid vapor pressure at 293 K and HPLC-FL instrument detection limits.

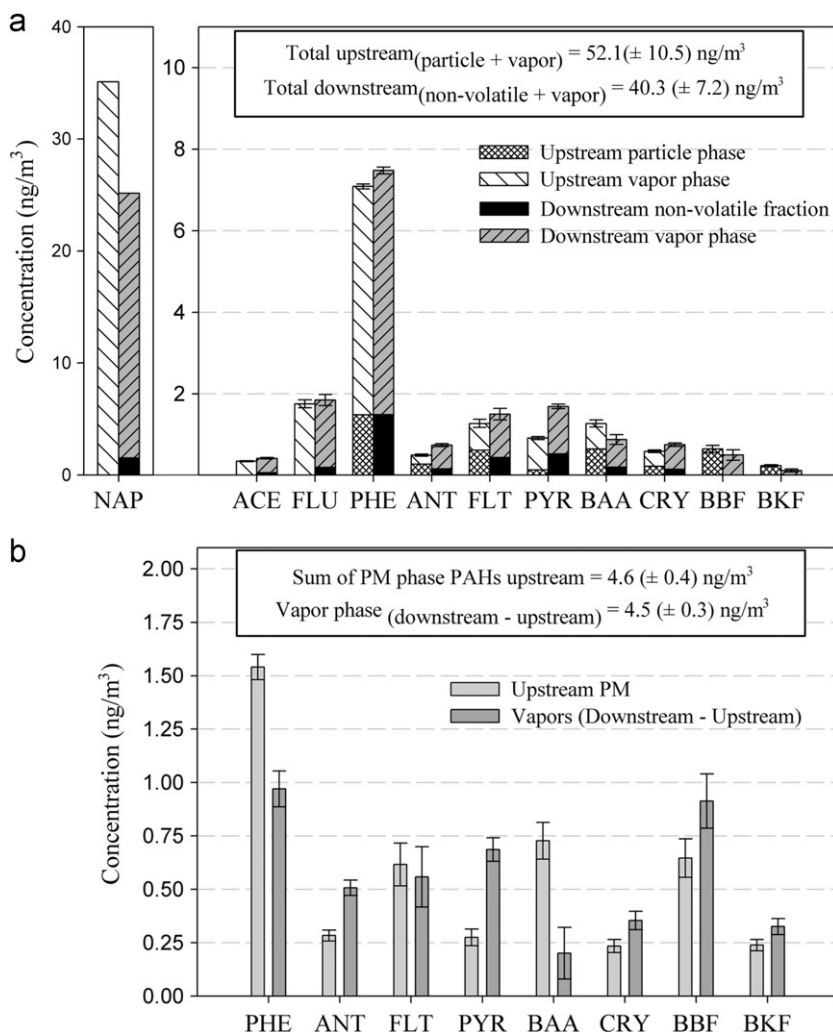
PAH	Code	MW	$P_L^0$ (atm)	IDL <sup>b</sup> (pg)
Naphthalene	NAP	128	2.98E–04	0.52
Acenaphthene	ACE	154	1.43E–05	0.16
Fluorene	FLU	166	6.63E–06	1.18
Phenanthrene	PHE	178	6.58E–07	0.72
Anthracene	ANT	178	5.91E–07	0.31
Fluoranthene	FLT	202	5.77E–08	1.29
Pyrene	PYR	202	3.33E–08	0.47
Benz[a]anthracene	BAA	228	3.20E–09	1.04
Chrysene	CRY	228	2.28E–09	0.37
Benzo[b]fluoranthene	BBF	252	2.33E–10	1.09
Benzo[k]fluoranthene	BKF	252	2.33E–10	0.32

<sup>a</sup> Data from Calvert et al. (2002).<sup>b</sup> Instrument Detection Limits from Eiguren-Fernandez et al. (2003).**Fig. 8.** Correlation between natural logarithm of the measured PAH concentrations upstream and natural logarithm of sum of the measured PAH concentrations downstream of the system and on the heater filter (non-volatile fraction).

vapor phase. The samples collected on the quartz filter immediately after the heater represent ideally non-volatile, particle phase PAHs, while those collected after the cooling section by the XAD sampler represent the sum of PAHs originally in the vapor phase plus the semi-volatile PAHs that evaporated from the particle phase during heating. The mass balance of PAHs was determined by comparing their total (i.e., PM plus vapor) concentrations measured upstream of the heater to the sum of the particle phase PAHs measured by the quartz filter placed immediately after the heater plus the vapor PAH concentrations measured by the XAD downstream of the cooling section.

Fig. 8 shows the linear regression plot between the total PAHs concentrations upstream and downstream of the VHF, including the 95% confidence intervals based on the standard deviations of our measurements. Natural logarithms were used to cover the wide range of measured concentrations, spanning roughly over 3 orders of magnitude (a linear regression plot would have been almost entirely driven by naphthalene concentrations, accounting for about 70% of the total measured PAH). The regression results demonstrated very good agreement in the PAH mass balance between the upstream and downstream total concentrations, with a slope of  $0.97 (\pm 0.22)$  and a regression coefficient ( $R^2$ ) value of 0.91, indicating limited overall diffusional loss of vapor phase PAHs to the walls of the cooling section, and efficient semi-volatile PAH recovery in the system, after heating and cooling sections.

The upstream and downstream PAH concentrations are also shown in Fig. 9a, with upstream concentrations segregated to PM-bound and vapor phase, whereas downstream concentrations are split into the non-volatile fraction, collected on the quartz filter immediately after the heater, and vapor phase PAH collected by the XAD sampler. The latter corresponds ideally to the upstream vapor phase PAHs plus the semi-volatile fraction of PAHs that evaporated from their particle phase after heating. The total (particle and vapor phase) PAHs concentration entering the VHF was  $52.1 (\pm 10.5) \text{ ng/m}^3$ , whereas the total concentrations measured on the quartz filter and XAD sampler downstream the VHF were  $4.5 (\pm 0.6)$  and  $40.3 (\pm 7.2) \text{ ng/m}^3$ , respectively.



**Fig. 9.** (a) Comparison of PAH concentrations measured upstream of the system in particle and vapor phase, PAH concentrations on the heater filter (the non-volatile fraction), and the recovered vapor phase PAHs measured after the cooling section and downstream of the system. The total (particle and vapor phase) PAHs concentrations entering the VHF were 52.1 (± 10.5) ng/m<sup>3</sup>, whereas the total concentrations measured on the quartz filter and XAD sampler downstream the VHF were 4.5 (± 0.6) and 40.3 (± 7.2) ng/m<sup>3</sup>, respectively. (b) Comparison of the upstream particle phase PAH concentrations (± standard error, SE) and the recovered vapor phase PAH concentrations (± SE), calculated by subtracting the upstream vapor phase concentration from the downstream vapor phase concentration of PAH species. The sum of particle phase concentrations of medium and high molecular weight PAHs entering the system was 4.6 ± 0.4 ng/m<sup>3</sup>, whereas their downstream minus upstream vapor concentrations were 4.5 ± 0.3 ng/m<sup>3</sup>.

The measured PM concentrations of the two- and three-ring PAHs (naphthalene, acenaphthene and fluorene) were below detection limit, as these low molecular weight PAHs are predominantly in vapor phase under atmospheric conditions, and were entirely adsorbed on XAD resins, with some small fraction (on average 6–7%) detected on the heater filter, likely due to adsorption. These low molecular weight PAHs accounted for about 73% (± 5%) of the total measured PAH, and were fully recovered downstream of the system, with some potential losses for NAP (Fig. 9a) possibly due to diffusion of NAP molecules on the walls of the system. The medium molecular weight PAHs (phenanthrene–chrysene) are present in both gas and particle phases in atmospheric conditions, with an average mass ratio of 29% in the particle phase, as measured upstream of VHF system. Following gas-particle repartitioning in the heater at 120 °C, the particle fraction decreased to 18% as measured downstream of heater, with the rest in vapor phase collected after cooling section. We defined the ratio of the downstream minus the upstream vapor phases PAH to the upstream particle phase concentration as the % recovery. Based on that definition, the total average recovery for medium molecular weight PAHs was 127.9% (± 31.8%). The higher molecular weight PAHs (i.e., benzo[b]fluoranthene and benzo[k]fluoranthene) are predominantly in particle phase and their gas phase concentrations upstream of the system were negligible. Similar to the medium molecular weight PAHs, their concentrations downstream of the system are entirely in the vapor phase, collected by the XAD sampler after they pass through the heating and cooling sections. The average recovery ratio of the high molecular weight PAHs was 138.9% (± 2.4%). The somewhat higher than 100% recovery for certain species may be due to some

underestimation of the particulate phase PAH upstream of the VHF due to volatilization losses from the upstream filter during sampling, which would lead to an overestimation of the ambient vapor phase of these PAH measured by the XAD sampler. The sum of particle phase concentrations of medium and high molecular weight PAHs entering the system was  $4.6 \pm 0.4 \text{ ng/m}^3$ , whereas their downstream minus upstream vapor concentrations were  $4.5 \pm 0.3 \text{ ng/m}^3$  after heating and cooling, with an overall recovery ratio of 99%.

It should be noted that in our field experiments discussed above, filter sampling was used to collect species in particulate phase, while XAD resin was used for vapor collection. These two methodologies represent the most commonly used approaches for organic PM and vapor sampling and chemical analysis. It was therefore assumed that the particulate and vapor phase PAH upstream of the VHF are properly captured by the filter and XAD samplers, respectively, and that the quartz filter in the heater captures only the non-volatile PM, without any gas phase adsorption, while the downstream XAD sampler collects only the vapor phase PAHs, including the volatile fraction that evaporates from their particle phase. However neither of these methodologies is artifact-free, and the interpretation of the results and the degree of the agreement between upstream and downstream PAH concentrations will thus need to be viewed with caution and treated with the appropriate caveats introduced by the lack of an ideal method for the collection and analysis of semi-volatile species. For example, we already see evidence of gas phase PAH adsorption on the quartz heater filter for PAH entirely partitioned in the vapor phase (Fig. 9a).

Nonetheless, the good overall agreement between the PAH concentrations measured upstream and downstream of the VHF and the reasonable overall PM recovery on the downstream XAD trap suggests that this system can be an attractive methodology for separating the particle and vapor phases of semi-volatile species and provide them for in-vivo exposure studies.

#### 4. Summary and conclusions

We have developed and evaluated experimentally a sampling system designed to provide concentrated semi-volatile particles and vapors for in-vivo exposure studies. Ambient particles are initially concentrated using the VACES and then drawn through a heater to remove semi-volatile species from the PM phase. The quartz filter downstream of the heater removes non-volatile particles while allowing semi-volatile vapors, initially bound to the PM phase, to pass through. The air stream is then cooled down to ambient temperatures without the occurrence of nucleation. Laboratory tests using ammonium sulfate, adipic acid and glutaric acid identified an optimum volatilization temperature setting ( $120^\circ\text{C}$ ), which maximizes the removal of semi-volatile vapors from the particulate phase, while avoiding nucleation of these species after cooling. Field experiments, in which the PM and vapor phase concentrations of selected polycyclic aromatic hydrocarbons (PAHs) were measured before and after the VHF system, showed in general very good recovery of the measured semi-volatile species in vapor phase. These results indicate that the modified VACES-heater-filter (VHF) system could provide separately concentrated PM (including their semi-volatile compounds), non-volatile PM (denuded of their semi-volatile species) by replacing the filter with active carbon cartridge in the denuder, using the original Dekati thermodenuder setup) and PM-bound semi-volatile species purely in their vapor phase for inhalation exposure studies. This technology makes it possible to conduct toxicity and inhalation exposure studies separately to the PM and vapor phases of semi-volatile organic pollutants in the urban atmosphere, and investigate the degree to which health effects attributable to these pollutants are affected by their phase. Given the dynamic behavior of these species in the atmosphere in terms of their partitioning between the PM and vapor phases, such investigations will become increasingly important.

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